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(54) Title: TIRES HAVING TREADS DERIVED FROM PARTICULATE CURED RUBBER

(57) Abstract

The resistance to tread wear of vehicule tires can be maintained or improved through the use of a tread rubber molding composition that includes from about 20 % to about 80 % by weight of a treated particulate rubber material. The latter material comprises cured rubber particules that have been surface treated with a liquid, sulfur-curable polymeric binder that has ethylenic unsaturation and that is soluble in benzene, hexane or both, the binder acting to soften the cured rubber particle surfaces to which it is applied.

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TIRES HAVING TREADS DERIVED FROM PARTICULATE CURED RUBBER

Field of the Invention

This invention relates to vehicle tires and particularly to treads for such tires.

Background of the Invention

Natural rubber and styrene-butadiene rubbers commonly are used in the manufacture of vehicle tires. Tire treads usually are of a polybutadiene rubber. The treads of new tires are formed during the tire molding process, whereas the treads of retreaded or "recapped" tires are formed by providing a layer of a virgin rubber molding composition circumferentially of the tire carcass and then subjecting the layer to molding to shape the tread and to form the tread grooves. The rubber molding material used for retreading may be a mixture of a natural or synthetic rubber (styrene-butadiene ("SBR")) containing an oil extender and a carbon black filler. To provide the tread with strength and reasonable wear resistance, virgin rubber materials are employed in both new and recapped treads.

My U.S. Patent 4,481,335, issued November 6, 1984, discloses a rubber composition derived from particles of scrap rubber that are surface treated with a liquid, curable polymeric binder. The surface-treated particulate material when added to virgin rubber stocks, provided moldable products.

Although the physical properties of the resulting products (tensile strength, elongation-to-break) were reduced, the ultimate products were nonetheless useful in situations which did not demand the ultimate physical properties normally associated with products molded from virgin rubber molding stocks.

Summary of the Invention

The invention relates to vehicle tires having treads molded from rubber molding compositions that contain substantial amounts of surface-treated particles of previously cured rubber. Surprisingly, although the tensile strength and ultimate elongation properties of the resulting treads are, as expected, poorer than properties resulting from the use of virgin rubber molding stocks, the ability of the tread to resist wear is at least as good as and often better than the resistance to tread wear exhibited by treads made from virgin rubber molding stocks.

In one embodiment, my invention relates to a vehicle tire having a tread portion that comprises the molded and cured product of a rubber molding composition containing from about 20% to about 80% by weight (and preferably from about 35% to about 75% by weight) of a treated particulate rubber material comprising cured rubber particles that have been surface-treated with a liquid, sulfur-curable polymeric binder having ethylenic unsaturation and that is soluble in benzene, hexane or both, the binder softening the cured rubber particle surfaces to which it is applied.

In another embodiment, my invention relates to a method of maintaining and often improving resistance to tread wear of a tire having a tread containing non-virgin rubber polymeric ingredients, the method

comprising the step of incorporating in a rubber molding composition from which the tread is to be molded from about 20% to about 80% by weight (and preferably from about 35% to about 75% by weight) of a treated particulate rubber material comprising cured rubber particles that have been surface treated with a liquid, sulfur-curable polymeric binder having ethylenic unsaturation and that is soluble in benzene, hexane, or both, the binder softening the cured rubber particle surfaces to which it is applied.

Detailed Description

The treated particulate rubber materials that are used in the invention include those described in my U.S. Patent 4,481,335, issued November 6, 1984, the teachings of which are incorporated herein by reference. Such treated particulate rubber compositions contain, as the major ingredient, cured rubber particles that are derived desirably from scrap tires through a grinding procedure. The particles may be of natural or synthetic rubber or combinations thereof, as used in the manufacture of tires. Such tires usually are of natural rubber or of SBR, although synthetic rubbers such as neoprene and nitrile rubbers, butyl rubbers and ethylene-propylene diene rubbers are satisfactory for use in the invention. The particles useful in the invention may range substantially in size, but will normally be in the range of about 20 to about 300 mesh (U.S. Sieve Series), with 30 mesh being currently considered as the preferred size range. It will be understood that "30 mesh" particles refers to particles that may have a variety of particle sizes but all of the particles being sufficiently small as to pass through a 30 mesh screen.

The polymeric binder which is employed is a liquid having a viscosity of 280° F of not greater than about 1,000,000 cp, and preferably is pourable at room temperature. The polymeric binder is characterized by ethylenic unsaturation, desirably containing at least three and preferably at least ten mole percent unsaturation. The binder is soluble in hexane or benzene or both to the extent of at least 10 grams of binder per 100 ml. of solvent at room temperature. The binder softens cured rubber particles to which it is applied; if a small piece of rubber scrap is thinly coated with a polymeric binder and then heated for ten minutes at 105° F, the surface of the rubber piece will soften and can be rubbed away by the fingers. This feature is particularly striking when the scrap rubber piece is carbon-filled; the removal of a surface layer of the piece leaves a dark stain on the fingers. The polymeric binder is itself sulfur curable to form a strong, solid article. A cured rubber patty made from equal parts of binder and sulfur, when cured at 310° F for 30 minutes, should be solid and strong.

Homopolymers and copolymers of 1,4-butadiene and substituted butadienes are preferred as the liquid binder. Copolymers of 1,4-butadiene and styrene have given excellent results. Reference is again made to my U.S. Patent 4,481,335 for an exemplary list of polymeric binders.

As curing agents for the treated, particulate rubber compositions used in the invention, sulfur and sulfur-containing materials are preferred. Elemental sulfur itself can be employed as a curing agent, as can various sulfur donor compounds. N-tert-butyl-2-benzothiazole sulfonamide, sold under the trademark "Santocure NS" by Monsanto Chemical Co.,

has given good results. The curing agent desirably is provided in an amount ranging from about 50% to about 500% by weight of the polymeric binder.

The treated particulate rubber materials employed in the invention may be produced by blending together in a suitable mixer such as a ribbon blender 100 parts by weight of cured rubber particles (e.g., particles derived as above from scrap tires), from about 1 to about 5 parts by weight, preferably from about 2 to about 4 parts by weight, of the polymeric binder, and an effective amount (ranging desirably from about 50% by weight to about 500% by weight based upon the weight of polymeric binder) of a curing agent such as sulfur or a sulfur donor. Blending is desirably performed at temperatures ranging from about 100° F. to about 280° F, until a substantially homogeneous, thorough particulate mixture is obtained. Substantially all of the cured rubber particles are thus very lightly coated with the polymeric binder, which appears to be absorbed into the surfaces of the particles. The particulate composition desirably is generally dry to the touch and is substantially free flowing.

In accordance with the invention, the treated particulate rubber material is blended with a virgin rubber stock before being molded as a tread of a vehicle tire. Virgin rubber stocks commonly include, per 100 parts of (uncured) virgin rubber, substantial amounts (e.g., 75 parts by weight) of a carbon black filler and up to 50 parts or more of an oil extender such as a high aromatic petroleum oil. Generally, the amounts of virgin rubber, carbon black and oil can be varied as desired. Blending of the treated particulate cured rubber material and the virgin

rubber stock can be performed as desired, using conventional equipment.

In the experiments that follow, in which tires were retreaded using conventional techniques, the virgin rubber composition was first banded on a rubber mill, following which the curing agent and then the treated particulate mixture were added to the mill batch. Mixing for each batch took about five minutes. The mixed blend was then removed as a continuous strip and cooled.

In the retreading operation, the blended, cooled strip was fed to an extruder ("Orbitread", Myer Tire Supply). Tire carcasses were prepared by buffing away the existing tread and coating the resulting surface with a rubber adhesive (Myer Tire Supply, V-10 "Orbibond"), which was allowed to dry. The tread composition was applied using an AMF "Tire Builder" CX-200, and the tire treads were then molded in standard presses at 147° C for 45 minutes. The same tread design was used for all tires. Initial tread depth in each case was 8.33 mm. The tires were trimmed and aged for a minimum of five days before being mounted upon vehicles for testing. Balancing was done at the time of mounting. Although initial road service testing was done with used tires, subsequent testing often utilized new tires since there was an indication that the experimental treads would outlast the used tire casings upon which they were placed.

In each of the examples reported below, the treated particulate material was derived from scrap tires ground to 30 mesh and surface coated by being mixed with a liquid comprising, per 100 parts of the particles, 3 parts of a liquid styrene-butadiene resin, 1-1/2 parts of elemental sulfur, and 0.75 parts

Santocure NS (Monsanto, above identified). The liquid styrene-butadiene resin was a clear amber liquid having a viscosity at 150° F of about 10,000 cp. The surface treated particles hereafter are sometimes referred to as "STP".

The experiements which follow employed three different standard virgin rubber stocks, each supplied by Copolymer Rubber and Chemical Company. The curing system used in each stock was a composition containing elemental sulfur, zinc oxide and other additives and sold by Production Systems, Inc. as "Curative SC-30-04". One virgin rubber stock, denoted "1847" contained a styrene-butadiene rubber having 23.5% bound styrene and including, per 100 parts of the rubber, 75 parts of carbon black and 50 parts of a high aromatic oil. Another virgin rubber stock, denoted "1849", contained slightly more carbon black and slightly more oil than the 1847 stock. Yet another virgin rubber stock, denoted "3652", contained less carbon black and less oil than the 1847 stock.

<u>Example I</u>

Steel belted radial tires were provided with treads formed from a composition containing 40% by weight of STP and 60% by weight of rubber stock 1849 to which had been added, per 100 parts of the stock, 2.5 parts of Curative SC-30-04. The tires were mounted as the rear drive tires of a 1971 Oldsmobile Cutlass. After 14,400 kilometers of driving, tread wear was measured at 1.98 millimeters. The vehicle had a history of wearing its rear tires nearly bald from driving 32,000 kilometers.

Example II

This example employed two used steel belted radial tire casings. One tire was retreaded with the 1849 virgin rubber stock to which had been added, per 100 parts of stock, 2-1/2 parts of the curative SC-30-04. The other tire was retreaded with a molding composition containing 60% by weight of the same 1849 stock and curative and containing 40% by weight of STP. The tires were mounted as the front tires of a 1980 Chevrolet Citation and driven for 17,600 kilometers. The tires were then transferred to the rear wheels and driven for an additional 23,360 kilometers. Close examination showed that the tires had identical tread wear of 3.18 mm, although the tire containing the STP showed more edge wear.

Example III .

Four new steel belted radial tires were retreaded with a retreading composition containing 40% by weight of STP and 60% by weight of the virgin rubber stock 1847 containing 2.5 parts of curative SC-30-04 per 100 parts of stock. All four tires were mounted on a 1983 Oldsmobile Diesel Custom Cruiser station wagon. Tread wear of each tire after 59,200 kilometers was measured at 3.97 mm. This vehicle usually had worn the treads of commercially available tires to near baldness after 64,000 kilometers.

Example IV

Two new steel belted radial tires were retreaded with a retreading composition comprising 50% by weight of virgin rubber stock 3652 (containing 2.6 parts of curative SC-30-04 per 100 parts of stock) and 50% by weight of STP. The tires were mounted as the rear tires on a Ford Bronco II which was used as a

delivery vehicle. This vehicle commonly had worn commercial tires to near baldness in 19,200-24,000 kilometers of driving. After 19,200 kilometers, the tires of this example were found to have a tread wear of 5.95 mm.

In each of the examples reported above, neither traction nor skid resistance of the experimental tires appeared to be affected.

Of substantial interest, the tires employing treads containing the STP appeared to run cooler than did control tires employing treads made from the same virgin stock but containing no STP. In one set of tests, after running at highway speeds for one to two hours at ambient temperatures greater than 27° C, differences in temperatures of the treads were measured by a pyrometer, and the treads containing the STP were found to have temperatures lower than the control tread temperatures by 5 C° or more.

Each of the tread compositions reported above were tested for hardness, tensile strength and elongation, the results being reported in the following table:

TABLE I

Composition	Durometer, Shore A	Tensile Strength, psi	Ultimate Elongation %
1849	60	2155	593
1849-60% STP- 40%	56	1547	390
1847	61	2057	486
1847-60% STP -40%	59	1592	400
1847-50% STP -50%	59	1585	387
0652	66	2096	460
3652-50% STP -50%	61	1531	380

It will be observed that the hardness, tensile strength and elongation of each of the rubber stocks was adversely affected by the addition of surface treated particles to the tread composition. Yet, the ability of the treads made from the surface treated particle compositions to resist tread wear was at least as good as that of treads produced from the virgin rubber stock alone. The excellent tread wear resistance resulting from the STP-containing tread compositions was unexpected but is highly desirable in that the invention provides yet another use for scrap tires and enables tires with good tread wear resistance to be manufactured from inexpensive materials derived from scrap tires.

While a preferred embodiment of the present invention has been described, it should be understood that various changes, adaptations and modifications may be made therein without departing from the spirit of the invention and the scope of the appended claims.

WHAT IS CLAIMED IS:

1. A vehicle tire having a tread portion comprising the molded and cured product of a rubber molding composition containing from about 20% to about 80% by weight of treated particulate rubber material comprising cured rubber particles surface treated with a liquid, sulfur-curable polymeric binder having ethylenic unsaturation and being soluble in benzene, hexane or both, the binder softening the cured rubber particle surfaces to which it is applied.

2. The vehicle tire of Claim 1 in which the treated particulate rubber material is present in the rubber molding composition at a concentration of from about 35% to about 75% by weight of the composition.

3. The vehicle tire of Claim 1 in which the sulfur-curable polymeric binder is a styrene-butadiene resin that is pourable at room temperature.

4. The vehicle tire of Claim 2 wherein the treated particulate rubber material is present in the tread molding composition at a concentration of from about 40% to about 50% by weight.

5. A method of manufacture of a vehicle tire having substantial resistance to tread wear, comprising the step of forming the tread of the tire from a rubber molding composition containing from about 20% to about 80% by weight of a treated particulate rubber material

comprising cured rubber particles surface treated with a liquid, sulfur-curable polymeric binder having ethylenic unsaturation and being soluble in benzene, hexane or both, the binder softening the cured rubber particle surfaces to which it is applied.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US87/02550

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC(4): B60C 1/00; B29D 30/06; C08J 11/04
US. CL. 152/209R; 156/128.1, 128.6; 264/37

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
U.S.	152/209R; 264/37, 331.13, 156/95, 96, 128.1, 128.6, 129 521/41, 43, 44.5, 45.5

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
X	US, A, 4,290,470 (WILLIAMS ET AL) 22 SEPTEMBER 1981, SEE COLUMN 2, LINES 11 TO 40 AND EXAMPLE 2.	1, 2, 5
X	US, A, 4,481,335 (STARK, JR.) 06 NOVEMBER 1984, SEE COLUMN 2, LINES 37 TO 55 AND 64 TO 68; COLUMN 4, LINE 65 TO COLUMN 5, LINE 13.	1-5
X	US, A, 2,378,717 (MACEY) 19 JUNE 1945, SEE THE ENTIRE DOCUMENT	1-5
A	US, A, 4,101,463 (MORGAN ET AL) 18 JULY 1978 SEE THE ENTIRE DOCUMENT	
A	US, A, 3,928,291 (SANDA, JR.) 23 DECEMBER 1975, SEE COLUMN 1, LINES 44 TO 48.	
A	US, A, 4,440,208 (TRICKEL ET AL) 03 APRIL 1984, SEE THE ENTIRE DOCUMENT.	

* Special categories of cited documents: [15]

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IV. CERTIFICATION

Date of the Actual Completion of the International Search [2]	Date of Mailing of this International Search Report [2]
19 NOVEMBER 1987	05 JAN 1988
International Searching Authority [1]	Signature of Authorized Officer [20]
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